

(12) UK Patent Application (19) GB (11)

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(43) Application published 25 Jun 1986

(21) Application No 8427288

(22) Date of filing 29 Oct 1984

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(51) INT CL⁴
C01B 3/22

(52) Domestic classification
(Edition H)
C5E 122 152 AS

(56) Documents cited
GB A 2139644

(58) Field of search
C5E
Selected US specifications from IPC sub-class C01B

(54) Producing synthesis gas

(57) High temperature gases leaving a reformer wherein hydrocarbons are converted to gases including oxides of carbon are mixed with carbon dioxide and passed through a catalyst promoting the reaction of carbon dioxide and hydrogen to carbon monoxide and water i.e. in a back shift converter. The stream leaving the converter may be passed through a carbon dioxide removal system, the carbon dioxide removed being heated and recycled to the exit of the reformer.

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SPECIFICATION

Process for the production of synthesis gas and its utilisation

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There are many areas of the world having cheap natural gas, much of which is flared because it is associated with oil production, and many companies are endeavouring to utilise such gas.

10 In the present state of the art there are two main means for converting the natural gas to raw synthesis gas: namely tubular steam reforming and, secondly, those processes utilising oxygen or an oxygen-containing gas, commonly referred to as partial oxidation or automatic processes.

15 In both the presently known processes the raw synthesis gas leaves the primary process unit at a very high temperature. The temperature is so high that very expansive means are needed to contain it, and thus it is usually cooled to a more manageable temperature by means of a waste heat boiler which generates a high pressure steam.

This process does not cool the very high temperature gases by the aforesaid means but adds to the very high temperature gases carbon dioxide, and then passes the resultant mixture through a catalyst which causes some of the carbon dioxide to react with hydrogen to form additional carbon monoxide. Inasmuch as the reaction of carbon monoxide with water to form carbon dioxide and hydrogen is commonly referred to as the water gas shift reaction, or just the shift reaction, the abovementioned reaction producing carbon monoxide from carbon dioxide may be referred to as back shifting.

25 There are a number of possible sources of the carbon dioxide which is added. The carbon dioxide may be that which could be removed from the effluent of the back shifting reactor. Normally this would be carried out after cooling of the gases, or the carbon dioxide may come from the removal of carbon dioxide from the natural gas feed, or the carbon dioxide may be imported, say from an ammonia or fermentation plant or from a carbon dioxide well, or carbon dioxide may be recovered from flue gas. Alternatively the carbon dioxide may be recovered from a stream which arises in the downstream processing of the effluent of the back shift reactor.

In this invention the carbon dioxide stream which is added to the very high temperature gases may contain other gases but preferably does not contain a high percentage of carbon monoxide or steam.

In the back shift reactor some of the carbon oxides may be methanated which reaction is very exothermic and such exotherm helps supply heat too. Indeed under certain circumstances the temperature during back shifting may even rise because there is an excess of heat release due to methanation over back shifting.

In the event that the carbon dioxide stream added to the very high temperature stream comes from a carbon dioxide removal unit which is located just downstream of the back shift reactor (after cooling) then the recovered CO₂ would probably be compressed and then recycled as above. This arrangement has the advantage both of supplying the necessary carbon dioxide for the back shift reaction and also removing

the carbon dioxide from the back shift reactor effluent, leaving a gas rich in carbon monoxide and hydrogen.

Should any carbon dioxide removal unit use a thermal regeneration process there is usually sufficient low grade heat to effect such regeneration from downstream processes.

As an alternative means of recovering the carbon dioxide a permeable membrane process such as Monsanto Prism Process may be used, for example, the effluent of the back shift reactor after cooling may be passed to such a unit whereupon, possibly after a preliminary hydrogen rich stream has been removed by a permeable membrane unit, a mixed carbon dioxide/hydrogen stream may be removed and this carbon dioxide/hydrogen rich stream may be the stream which is recycled to the very high temperature stream. In this case the presence of hydrogen has an advantageous effect in that it moves the equilibrium of the reaction back towards carbon monoxide, although care must be taken to ensure that it does not simultaneously cause too much methanation, which in turn would result in a loss of carbon monoxide, and indeed a very high heat release.

The effluent from the back shift reaction, preferably after CO₂ removal and preferably after adjusting the hydrogen/carbon monoxide ratio by means such as a permeable membrane process or a pressure swing adsorption process, may then be utilised from synthesis processes such as Fischer-Tropsch, and OXO alcohols. For such processes the hydrogen/carbon monoxide ratio would be above .5.

Alternatively, after carbon dioxide removal the carbon monoxide content in the gas may be recovered by means such as a selective solvent processes such as the Cosorb process, or by means of pressure swing adsorption, or by cryogenic means.

In this invention feedstock has been referred to as natural gas but a wide range of hydrocarbon materials may be used, including ethane.

In this application there is provided an invention characterised by

A. the reforming of a hydrocarbon to gases, including oxides of carbon

B. the addition of a carbon dioxide containing gas to the hot effluent from A

C. passing the mixture through a catalyst promoting the reaction of carbon dioxide and hydrogen to carbon monoxide and water.

CLAIMS

1. A process characterised by:

A. the reforming of a hydrocarbon to gases, including oxides of carbon

B. the addition of a carbon dioxide containing gas to the hot effluent from A.

C. passing the mixture through a catalyst promoting the reaction of carbon dioxide and hydrogen to carbon monoxide and water.

2. A process as claimed in claim 1 wherein the carbon dioxide containing gas is recovered from the effluent of the back shifted reactor.

3. A process as claimed in claim 1 wherein the carbon dioxide containing gas is recovered by removing it from the hydrocarbon feed.

4. A process as claimed in claim 1 wherein carbon dioxide is supplied from a well or a carbon dioxide

producing process such as an ammonia plant or a fermentation process.

5. Products produced from gases produced from the aforementioned processes.

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New claims or amendments to claims filed on 13 Feb '86.

Superseded claims 1 only.

10 CLAIMS

1. A process characterised by:

A. the reforming of a hydrocarbon to gases, including oxides of carbon

B. the addition of a carbon dioxide containing gas to

15 the hot effluent from A

C. passing the mixture through a catalyst promoting the reaction of carbon dioxide and hydrogen to carbon monoxide and water but which does not promote the formation/decomposition of methane.

20 2. A process as claimed in claim 1 wherein the carbon dioxide containing gas is recovered from the effluent of the back shifted reactor.

3. A process as claimed in claim 1 wherein the carbon dioxide containing gas is recovered by remov-

25 ing it from the hydrocarbon feed.

4. A process as claimed in claim 1 wherein carbon dioxide is supplied from a well or a carbon dioxide producing process such as an ammonia plant or a fermentation process.

30 5. Products produced from gases produced from the aforementioned processes.